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PROCESS FOR PREPARING POLYURETHANES THEREFROM

## (57) Abstract

This invention relates to polyurethane polymers, particularly polyurethane elastomeric polymers, prepared from isocyanate-reactive compositions comprising a polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and containing a total of from 10 to 40 weight percent polymerized ethylene oxide wherein the ethylene oxide is distributed as a plurality of internal polyoxyethylene blocks having a molecular weight of from 176 to 600, and a polyoxyethylene cap representing from 5 to 25 percent of the total polymerized ethylene oxide present in the polyol. Use of such polyols provides for polymers exhibiting desirable physical properties including good abrasion wear resistance.

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-1-

POLYOXYALKYLENE POLYOLS CONTAINING INTERNAL  
POLYOXYETHYLENE BLOCKS AND A PROCESS FOR PREPARING  
POLYURETHANES THEREFROM

This invention relates to polyoxyalkylene polyols containing internal polyoxyethylene blocks and a process for preparing polyurethanes therefrom.

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It is well-known to prepare elastomeric polyurethane polymers by reacting an organic polyisocyanate with an isocyanate-reactive composition comprising a polyether polyol or a polyester polyol.

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Resulting polymers obtained from polyester polyol have attractive physical properties, but may only be prepared under often difficult and undesirable process conditions. Polyester polyols are frequently highly viscous liquids or low melting point solids at room temperature. It is therefore necessary to conduct such processes employing polyester polyols at an elevated temperature or employ specialized equipment capable of handling high viscosity components.

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Generally easier processing is associated with use of polyether polyols when preparing elastomeric polyurethane polymers. U.S. Patent 4,440,705 discloses the use of polyether polyols in the preparation of poly-

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-2-

urethane elastomers. The polyether polyols described are polyoxypropylene polyols end-capped with polyoxyethylene blocks. The polyoxyethylene blocks are present in such concentrations to provide sufficient primary hydroxyl content allowing for high reactivity and short mold cycle times.

However, to obtain polyether polyol-based polyurethane elastomers which have similar properties to those prepared from polyester polyols, especially with respect to resistance to abrasive wear, it is generally necessary to use polyols having an extended polyoxyethylene end-cap. However, in this case undesirable polar interactions may be encouraged leading to turbidity of the polyether polyol. The presence of turbidity is disadvantageous as it can cause processing difficulties in preparing the elastomer and provide an elastomer with inferior physical properties. Such polyether polyols, as polyester polyols, can also require high processing temperatures as turbidity frequently is associated with higher viscosities. Incorporation of ethylene oxide, or oxyethylene residues, into a polyether polyol for the purpose of enhancing properties of polyurethane elastomers prepared therefrom is also known from other publications.

In Canadian Patent 1,133,650 it is taught to prepare copolymer polyols with polyoxypropylene-oxyethylene base polyols where the ethylene oxide is distributed internally within the oxyalkylene chain and as a terminal oxyethylene cap. The internal ethylene oxide is taught as providing for solubility of the chain-extending agent and the terminal oxyethylene cap providing for required processibility characteristics

and physical properties of the resulting elastomeric polymer.

In the published patent specification, GB 1,063,278 it is taught to prepare elastomeric polyure-  
5 thanes from polyether polyols having a hydroxyl equivalent weight of from 3400 to 8000 and containing butylene oxide and from 10 to 50 weight percent ethylene oxide distributed randomly. The resulting elastomers are disclosed as having enhanced abrasion resistance,  
10 low hardness and low temperature properties compared to elastomers prepared from lower equivalent weight polyether polyols.

However, the incorporating of ethylene oxide  
15 into a polyether polyol for use in elastomeric polymer preparation has some disadvantages. The ethylene oxide content provides a more polar polyol which has a greater hygroscopic tendency and therefore the corresponding elastomeric polymers obtained therefrom frequently  
20 display similar characteristics. Such polymers are susceptible to hydrolysis and are therefore unsuitable for applications where prolonged exposure to humid conditions may occur.

25 It is therefore desirable to prepare an elastomeric polyurethane polymer from a polyether polyol that provides for optimum abrasion resistance properties and yet which is a clear, low viscosity liquid allowing for  
30 good processability at, for example, room temperature. It is further desirable that such a polyether polyol provides for similar or improved physical properties as for existing polymers.

We have now discovered that elastomeric polyisocyanate-based polymers having satisfactory humid aging characteristics and improved abrasion resistance properties can be prepared by a process using polyoxyalkylene polyols which are clear, low viscosity liquids, conferring good processability at room temperature. Such polyoxyalkylene polyols are characterized in that they have an average hydroxyl equivalent weight of from about 800 to about 3000 and contain a plurality of internal polyoxyethylene blocks of specific molecular weight in addition to a terminal polyoxyethylene cap.

In one aspect, this invention is a polyurethane polymer prepared by intimately mixing under reaction conditions an organic polyisocyanate with an isocyanate-reactive composition wherein the ratio of polyisocyanate to isocyanate-reactive composition is such so as to provide an average of from 0.9 to 1.25 isocyanate groups per active hydrogen atom present in the isocyanate-reactive composition which comprises at least one polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and containing polymerized ethylene oxide in an amount of from 10 to 40 weight percent by total weight of the polyoxyalkylene polyol and characterized in that

(a) the polyoxyalkylene polyol contains at least two internal polyoxyethylene blocks having a molecular weight of from 176 to 600; and

(b) the polyol contains a polyoxyethylene end-cap which is from 5 to 25 weight percent of

-5-

total polymerized ethylene oxide present in the polyol.

In a second aspect, this invention is a polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and which comprises polymerized ethylene oxide in an amount of from 10 to 40 weight percent and characterized in that

(a) the polyoxyalkylene polyol contains at least two internal polyoxyethylene blocks having a molecular weight of from 176 to 600; and

(b) the polyol contains a polyoxyethylene end-cap which is from 5 to 25 weight percent of total polymerized ethylene oxide present in the polyol.

In a third aspect, this invention relates to a process for preparing a polyurethane polymer having an average density of from 200 to 700 kg/m<sup>3</sup> employing a polymer-forming composition comprising

(a) a polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and constituted by polymerized ethylene oxide in an amount of from 10 to 40 weight percent and characterized in that

(i) the polyoxyalkylene polyol contains at least two internal polyoxyethylene blocks having a molecular weight of from 176 to 600; and

-6-

(ii) the polyol contains a polyoxyethylene end-cap which is from 5 to 25 weight percent of total polymerized ethylene oxide present in the polyol;

5 (b) a chain-extending agent, having a molecular weight of less than or equal to 250, in an amount of from 2 to 40 parts by weight per 100 parts by total weight of polyol including (a) present;

10 (c) an effective amount of a blowing agent; and

15 (d) an isocyanate-terminated 4,4'-methylene diphenyldiisocyanate prepolymer in an amount to provide from 0.9 to 1.25 isocyanate groups per isocyanate-reactive hydrogen atom present in the polymer-forming composition.

20 Surprisingly it has been found that by distributing the ethylene oxide within the polyol as described above, it allows for the formation of polyoxyalkylene polyols which are clear low viscosity products. Further, it is shown that, surprisingly, the use of such polyoxyalkylene polyols in preparing elastomeric polymers provides for good abrasion resistance properties. The improved abrasion resistance properties are thought to result from the enhanced cohesive interactions within the polymeric structure obtained through the incorporating of such internal polyoxyethylene blocks into the polyether polyol.

25 The polymer prepared by the process of this invention can be characterized in that it exhibits

-7-

abrasion resistance properties as measured according to test procedure DIN 53516 where the observed weight loss is from 325 mg or less, preferably from 300 mg or less, more preferably from 250 mg or less and most preferably from 200 mg or less.

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The polymer of this invention is prepared by intimately mixing under reaction conditions a mixture comprising an organic polyisocyanate and an isocyanate-reactive composition. The isocyanate-reactive composition comprises at least one polyoxyalkylene polyol having a plurality of internal polyoxyethylene blocks and being end-capped with polymerized ethylene oxide.

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The polyoxyalkylene polyol is characterized in that it has an average hydroxyl equivalent weight of from 800 to 3000, preferably from 1000 to 2500, and more preferably from 1500 to 2000. The polyol is further characterized in that it contains from 10 to 40, preferably from 15 to 40, and more preferably from 20 to 40 weight percent by total weight of the polyol, polymerized ethylene oxide.

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To achieve the desirable physical properties particularly for abrasion and humid aging performance of elastomeric products prepared from the polyoxyalkylene polyol, it has been discovered that it is necessary to have the polymerized ethylene oxide distributed in a specific manner. The polymerized ethylene oxide content is distributed within the polyol as an internal polyoxyethylene block and as a terminal, or cap, polyoxyethylene block. Preferably, the polyol contains at least two independently distinct internal polyoxyethylene blocks. No upper limit to the number of

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-8-

internal polyoxyethylene blocks exists other than the constraints imposed by the total polymerized ethylene oxide content of the polyol and the size of the internal block as discussed hereafter.

5           The molecular weight of each internal polyoxyethylene block is from 176 to 600, preferably from 220 to 528, and more preferably from 308 to 440. If the molecular weight of the internal block is less  
10           than or greater than this range, the improved abrasion resistance or maintenance of physical properties may not be obtained. Further, if the molecular weight of the block exceeds 600, depending on the end equivalent weight of the polyol and total ethylene oxide content,  
15           the resulting polyol may be turbid.

          The quantity of polymerized ethylene oxide present as an end-cap on the polyol is from 5 to 25, preferably from 15 to 25, and more preferably from 18 to  
20           22 weight percent by total weight of the polyol. The end-cap is necessary to provide the polyol with sufficient primary hydroxyl character allowing for a satisfactory balance between polyol reactivity and visco-elastic properties when preparing the polymer. As  
25           with the internal polyoxyethylene block, if the size of the polymerized ethylene oxide end-cap becomes too great for a given polyol equivalent weight, the product may become turbid and/or solid.

30           Each internal polyoxyethylene block is separated from other like internal blocks and/or the terminal polyoxyethylene block by a bridging polyoxyalkylene block consisting essentially of C<sub>3</sub> or higher oxyalkylene units. Such a bridging polyoxyalkylene block advantageously has a molecular

weight of from at least 58, preferably from at least 116 and more preferably from at least 174. Exemplary of such C<sub>3</sub> or higher oxyalkylene units include propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, epichlorohydrin, trichlorobutylene oxide and mixtures thereof. Preferably, the bridging polyoxyalkylene block consists essentially of polymerized propylene oxide.

The polyoxyalkylene polyol is prepared by reacting an initiator with alkylene oxides. The initiator or mixture of initiators containing an average of at least 1.7; preferably from 1.8 to 4, more preferably from 1.8 to 3 and most preferably 1.8 to 2.2 active hydrogen atoms per molecule. Use of such initiators provides for a like functionality of the resulting polyol.

For the purpose of this invention, active hydrogen atoms are defined as those hydrogens which react positively in the Zerewitinoff test, see Kohler, *J. Amer. Chem. Soc.*, Vol. 49, p. 3181 (1927). Representative of groups containing such active hydrogen atoms are -OH, -COOH, -SH and -NHR where R can be hydrogen, alkyl, cycloalkyl, or aryl aromatic.

Exemplary of suitable initiators bearing such active hydrogen atoms are polyols, polyether adducts of polyols, polyamines and other compounds having a plurality of active hydrogen atoms per molecule, such as are described in column 2 of U.S. Patent 4,500,422.

Preferred initiators for use in preparing the polyoxyalkylene polyol employed within this invention are ethylene glycol, propylene glycol, butylene glycol, glycerine, 1,1,1-trimethylolpropane, 1,1,1-trimethylol-

-10-

ethane,  $\alpha$ -methylglucoside, C<sub>2-8</sub> alkylene diamines such as, for example, ethylenediamine and hexamethylenediamine, and mixtures thereof. Especially preferred are the glycol initiators or alkoxyated adducts of such glycols and especially propoxylated glycols.

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Suitable processes for the preparation of the polyoxyalkylene polyols are such as, for example, disclosed by Wurtz in 1859 (see *Encyclopedia of Chemical Technology*, Vol. 7, pp. 257-262, published by Interscience Publishers, Inc. (1951)) or U.S. Patents 1,922,459 and 3,040,076. Generally, the alkylene oxide(s) is polymerized at pressures above atmospheric pressure with an initiator in the presence of a strongly basic material such as an alkali metal hydroxide or tertiary amine acting as an alkoxylation catalyst. Suitable catalysts include potassium hydroxide, sodium hydroxide and barium hydroxide with barium hydroxide being preferred because it allows for the convenient manufacture of high equivalent weight products with low levels of unsaturation.

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In addition to the polyoxyalkylene polyol, the isocyanate-reactive composition advantageously comprises a chain-extending agent. The term "chain-extending agent" as used herein represents an organic compound, generally a difunctional compound having a molecular weight of 250 or less and preferably 200 or less. Exemplary of suitable chain-extending agents are glycols, aliphatic diamines, aromatic diamines and mixtures thereof. Preferred chain-extending agents include the glycols such as, for example, ethylene diol, 1,3-propylene diol, 1,6-hexane diol and especially 1,4-butanediol. Additional compounds suitable as chain-

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-extending agents are described in columns 5 and 6 of U.S. Patent 4,500,442.

The amount of chain-extending agent present in the isocyanate-reactive composition depends on its molecular weight and the physical properties desired for the resulting polymer. Greater mole quantities of chain-extending agent generally provide for polymers which are harder and exhibit, for example, higher heat distortion temperatures. Typically, the chain-extending agent will be present in an amount of from 2 to 40, preferably from 2 to 30, and more preferably from 5 to 20 parts by weight per 100 parts of total weight of all polyols, including the polyoxyalkylene polyol, present.

Combinations of chain-extending agents, especially dihydroxyl compounds, may be used to enhance certain processing properties such as, for example, flowability of the reacting mixture when preparing molded articles.

Further to the polyoxyalkylene polyol and chain-extending agent present in the isocyanate-reactive composition, the composition optionally may contain additional polyol components characterized by the absence, within their structure, of internal blocks of polymerized ethylene oxide having a molecular weight of from 176 to 600.

Polyols suitable for use as the optional component when preparing elastomeric polymers are those typically having hydroxyl equivalent weights from 800 to 3000 and may be a polyester polyol but more preferably are a polyether polyol. Illustrative of such polyols are the polyether polyols sold by The Dow Chemical

-12-

Company under the trademark "VORANOL™" and include VORANOL™ EP 1900 and VORANOL™ CP 6001.

When the isocyanate-reactive composition comprises the polyoxyalkylene polyol in combination with an optional polyol, the polyoxyalkylene polyol is present in a quantity sufficient to obtain the improved abrasion resistance properties. Generally, such quantity is from 50 to 99, preferably from 60 to 99 and more preferably from 60 to 90 weight percent of the total weight of polyoxyalkylene polyol and optional polyol present. When using combinations of the polyoxyalkylene polyol and optional polyol, it is advantageous for the physical properties of the resulting elastomer if the total oxyethylene, polymerized ethylene oxide, content of such a mixture is from 10 to 40, preferably from 20 to 40 and more preferably from 30 to 40 weight percent.

The organic polyisocyanate used in this invention advantageously has an average isocyanate functionality of from 1.8 to 2.7, and preferably from 1.9 to 2.4. Use of isocyanates having functionalities outside these limits may not provide an elastomeric polymer of quality. Suitable polyisocyanates include aliphatic and aromatic polyisocyanates. Such polyisocyanates are described, for example, in U.S. Patents 3,001,973; 3,124,605; 3,152,162; 3,394,164; 3,401,180; 3,454,606; 3,492,330 and 4,065,410.

Aromatic polyisocyanates useful herein include 2,4- and/or 2,6-toluene diisocyanate, 2,4'- and 4,4'-diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate, polymethylene polyphenyl polyisocyanates, or mixtures thereof.

-13-

Prepolymers and quasi-prepolymers of the above-mentioned polyisocyanates are useful herein. Such prepolymers will typically have an isocyanate content of from about 0.5 to about 48 percent, preferably from about 5 to about 25 percent and more preferably from about 15 to about 25 percent by weight isocyanate groups. The prepolymers can be prepared by processes well-known to those skilled in the art. Typically, the prepolymers are prepared by reacting a stoichiometric excess of the polyisocyanate with an active hydrogen-containing material.

The preferred isocyanates for preparing the polymers of this invention are aromatic polyisocyanates and preferably an aromatic diisocyanate comprising 4,4'-diphenylmethane diisocyanate or derivatives thereof, especially prepolymers. Advantageously, the aromatic polyisocyanate comprises at least 50, and preferably at least 70 weight percent of 4,4'-diphenylmethane diisocyanate.

The quantity of polyisocyanate employed in the preparation of the polymer of this invention is sufficient to react with all the isocyanate-reactive, active hydrogen atoms present in the isocyanate-reactive composition including water, if present. Advantageously, there is sufficient polyisocyanate present to provide from 0.9 to 1.25, preferably from 0.95 to 1.15, and more preferably from 0.97 to 1.05 isocyanate groups per active hydrogen atom present in the isocyanate-reactive composition.

Additives such as catalysts, blowing agents, surfactants, fillers, pigments, antioxidants, and anti-static agents can also be present when preparing the

-14-

polymer of this invention. The use of such additives is well-known in the art and reference is made thereto for this purpose.

Suitable catalysts include the tertiary amine and organometallic compounds such as described in U.S. Patent 4,065,410. When making the polymers of this invention, it is preferred to have catalysts present. Generally, from 0.01 to 2, preferably from 0.01 to 1.0 part of catalyst is employed per 100 parts of isocyanate-reactive composition. Particularly useful catalysts are dibutyltin laurate, triethylenediamine and bis(dimethylaminoethyl)ether.

Blowing agents which are useful in preparing polymers having a cellular structure and a reduced overall polymer density include non-reactive, volatile, organic compounds and/or water, the latter which reacts with isocyanate groups to generate carbon dioxide. The blowing agent(s) are employed in an amount to provide the elastomeric polymer having an overall density typically of from 200 to 700, preferably from 250 to 600 and more preferably from 250 to 550 kg/m<sup>3</sup>. Such elastomeric polymers are of value in applications where the use of lower density materials is desirable such as, for example, shoe soles.

The amount of water which may be used depends on the desired density of the polymer but is advantageously from 0.05 to 2 weight percent based on the weight of isocyanate-reactive composition. Other suitable blowing agents are low boiling liquids, generally organic compounds, which evaporate under the influence of the reaction temperature. Such boiling agents generally have a boiling point below 100°C and

include halogenated hydrocarbons such as methylene chloride, trichlorofluoromethane, dichlorodifluoromethane, dichlorofluoromethane, dichlorotetrafluoroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloroethane, 1,1,1--trichlorodifluoroethane, and  
5 1,1,1-trichlorofluoroethane. Mixtures of these low boiling liquids with each other and/or with substituted or unsubstituted hydrocarbons may be used. Typically, such blowing agent(s) are used in amounts of from 0.1 to  
10 10 weight percent based on the total weight of isocyanate-reactive composition, to provide polymers of the desired density.

Suitable pigments and fillers include carbon  
15 black, titanium dioxide, iron oxide, calcium carbonate, alum, clays such as kaolin or wollastonite, prepared glass fibers chopped or continuous, polyesters and other polymeric fibers.

Suitable antistatic agents which may be  
20 employed are ionizable metal salts such as described in U.S. Patent 4,617,325.

The polymer of this invention can be prepared  
25 by a one-shot method according to the known reaction injection molding techniques, such as described in, for example, *Polyurethanes Handbook* by Günter Oertel, Hanser Publishers (Munich) ISBN 0-02-948920-2 (1985).

The polymer of this invention is preferably a  
30 cast elastomer. Such a polymer is advantageously prepared by mixing the reaction components at room temperature or a slightly elevated temperature and then pouring the reaction mixture into a heated mold which is subsequently closed. The reaction mixture, on reacting

-16-

out, takes the shape of the mold to produce a polyurethane polymer of a predesigned structure, which can then, when sufficiently cured, be removed from the mold.

Suitable conditions for curing, when a cast polymer is formed, include a mold temperature typically of from 20°C to 170°C, preferably from 35°C to 75°C, which results in a cure time of from 2 to between 10 minutes. Optimum cure conditions will depend additionally on the particular components including catalysts and quantities used in preparing the polymer and the size and shape of the article prepared.

The elastomeric polymer of this invention is useful in the preparation of articles such as rollers, hammers, pipe liners, gears, pump chambers, wheels, impellers, door seals, coatings, tires, shoe soles, wiper blades, gaskets and belts. When the polyurethane polymer of this invention is a foam, it is useful in the preparation of upholstery materials, mattresses, packing materials and insulation for sound or heat.

The following examples are provided to illustrate the invention but are not intended to limit the scope thereof. All parts and percentages are given by weight unless otherwise indicated.

The physical properties of the polyoxyalkylene polyols and elastomers where reported are observed according to the following procedures.

Polyol analysis: hydroxyl number and equivalent weight - ASTM D-4274; viscosity - ASTM D-445; unsaturation - ASTM D-4671.

Elastomer analysis; abrasion resistance - DIN 53516; tensile strength and elongation - DIN 53504; flexural fatigue - DIN 53522 and hardness - DIN 53505.

Example 1

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This example illustrates the preparation of a 2000 equivalent weight polyoxyalkylene polyol containing two internal polyoxyethylene blocks each having a theoretical molecular weight of 396 and containing in total 10 39.6 weight percent polymerized ethylene oxide, of the total 20 weight percent is present as a terminal polyoxyethylene block.

15 In a suitable reactor capable of operating at pressure from about 0.01 atm to about 10 atm, an initiator mixture comprising 800 parts of a poly(oxypropylene) diol having an equivalent weight of 200 and 56 parts of potassium hydroxide is prepared. The potassium hydroxide is added as an aqueous solution (45 percent by 20 weight).

The resulting mixture is stirred at approximately 60°C for about one hour, the temperature is then increased to about 100°C and a vacuum applied to remove 25 the water. When the water content of the initiator mixture as observed by Karl Fischer titrometric analysis is less than 1500 ppm, the temperature is increased again to 115°C.

30

To the initiator mixture at 115°C is added while stirring 1584 parts ethylene oxide at an addition rate such to maintain a constant pressure within the reactor of from 3.5 to 5.0 atmospheres.

-18-

When the ethylene oxide feed is complete, the resulting reaction product is stirred at about 115°C until the pressure within the reactor is constant with time, typically from one to two hours. The contents of the reactor are then cooled to about 95°C and 4032 parts  
5 of propylene oxide added at an addition rate of about 1000 parts/hour. When the propylene oxide addition is complete, the reactor temperature is increased to about 100°C, and maintained while stirring until a constant  
10 internal reactor pressure with time is observed, in this example approximately five hours.

The contents of the reactor are then heated to about 115°C and a further 1584 parts of ethylene oxide  
15 added at an addition rate of about 800 parts/hour. When the feed is complete, the reactor contents are stirred at about 115°C for a further one to 2 hours or until a constant pressure with time is observed.

20 The potassium content of the crude polyol is removed by treating with magnesium silicate, to give a finished product.

The finished product is characterized in that  
25 it has a hydroxyl number of 28, a viscosity of 529 cst (25°C), 0.047 meq/g unsaturation and a primary hydroxyl content of about 90 percent as determined by nuclear magnetic resonance.

30 Example 2

A polyoxyalkylene polyol having an equivalent weight of 2000 and containing two internal polyoxyethylene blocks each having a molecular weight of 308 and containing in total 34.8 weight percent polymerized

-19-

ethylene oxide, of the total 19.5 weight percent is present as a terminal polyoxyethylene block.

5 In a suitable reactor capable of operating at pressure from about 0.01 atm to about 10 atm, an initiator mixture comprising 800 parts of a poly(oxypropylene) diol having an equivalent weight of 200 and 56 parts of potassium hydroxide is prepared. The potassium hydroxide is added as an aqueous solution (45 percent by weight).

10

The resulting mixture is stirred at approximately 60°C for about one hour, the temperature is then increased to about 100°C and a vacuum applied to remove the water. When the water content of the initiator mixture is less than 1500 ppm, the temperature is increased to about 115°C.

15

To the initiator mixture at 115°C is added while stirring 1232 parts ethylene oxide at an addition rate such as to maintain a constant pressure within the reactor of from 3.5 to 5.0 atmospheres.

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When the ethylene oxide feed is complete, the resulting reaction product is stirred at about 115°C until the pressure within the reactor is constant with time, typically from one to two hours. The contents of the reactor are then cooled to about 95°C and 4480 parts of propylene oxide added at an addition rate of about 1000 parts/hour. When the propylene oxide addition is complete, the reactor temperature is increased to about 100°C, and maintained while stirring until a constant internal reactor pressure with time is observed, in this example, approximately five hours.

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-20-

5 The contents of the reactor are then heated to about 115°C and a further 1584 parts of ethylene oxide added at an addition rate of about 800 parts/hour. When the feed is complete, the reactor contents are stirred at about 115°C for a further one to 2 hours or until a constant pressure with time is observed.

10 The potassium content of the crude polyol is removed by treating with magnesium silicate, to give a finished product.

15 The finished product is characterized in that it has a hydroxyl number of 28.4, a viscosity of 489 cst (25°C), an unsaturation content of 0.061 meq/g and a primary hydroxyl content of greater than 90 percent as observed by nuclear magnetic resonance.

### Example 3

20 A polyoxyalkylene polyol having an equivalent weight of 2000 and containing two internal polyoxyethylene blocks each having a molecular weight of 220 and containing in total 30 weight percent polymerized ethylene oxide, of the total 19.3 weight percent is present as a terminal polyoxyethylene block.

25 In a suitable reactor capable of operating at pressure from about 0.01 atm to about 10 atm, an initiator mixture comprising 800 parts of a poly(oxypropylene) diol having an equivalent weight of 200 and 56 parts of potassium hydroxide is prepared. The potassium hydroxide is added as an aqueous solution (45 percent by weight).

30 The resulting mixture is stirred at approximately 60°C for about one hour, the temperature is then

-21-

increased to about 100°C and a vacuum applied to remove the water. When the water content of the initiator mixture is less than 1500 ppm, the temperature is increased again to 115°C.

5           To the initiator mixture at 115°C is added while stirring 880 parts ethylene oxide at such an addition rate such as to maintain a constant pressure within the reactor of from 3.5 to 5.0 atmospheres.

10           When the ethylene oxide feed is complete, the resulting reaction product is stirred at about 115°C until the pressure within the reactor is constant with time, typically from one to two hours. The contents of the reactor are then cooled to about 95°C and 4928 parts  
15 of propylene oxide added at an addition rate of about 1000 parts/hour. When the propylene oxide addition is complete, the reactor temperature is increased to about 100°C, and maintained while stirring until a constant  
20 internal reactor pressure with time is observed.

          The contents of the reactor are then heated to about 115°C and a further 1584 parts of ethylene oxide added at an addition rate of about 800 parts/hour. When  
25 the feed is complete, the reactor contents are stirred at about 115°C for a further one to 2 hours or until a constant pressure with time is observed.

          The potassium content of the crude polyol is  
30 removed by treating with magnesium silicate, to give a finished product.

          The finished product is characterized in that it has a hydroxyl number of 27.7, a viscosity of 463 cst (25°C), an unsaturation content of 0.054 meq/g and a

-22-

primary hydroxyl content of greater than 90 percent as observed by nuclear magnetic resonance.

Example 4

5           A polyoxyalkylene polyol having a hydroxyl  
equivalent weight of 2500 and containing two internal  
polyoxyethylene blocks each having a molecular weight of  
396 and containing in total 30.9 weight percent polymer-  
10 is present as a terminal polyoxyethylene block.

          In a suitable reactor capable of operating at  
pressure from about 0.01 atm to about 10 atm, an initi-  
ator mixture comprising 800 parts of a poly(oxypropyl-  
15 ene) diol having an equivalent weight of 200 and 56  
parts of potassium hydroxide is prepared. The potas-  
sium hydroxide is added as an aqueous solution (45  
percent by weight).

20           The resulting mixture is stirred at approxi-  
mately 60°C for about one hour, the temperature is then  
increased to about 100°C and a vacuum applied to remove  
the water. When the water content of the initiator  
mixture is less than 1500 ppm, the temperature is  
25 increased to about 115°C.

          To the initiator mixture at 115°C is added while  
stirring 1584 parts ethylene oxide at an addition rate  
such to maintain a constant pressure within the reactor  
30 of from 3.5 to 5.0 atmospheres.

          When the ethylene oxide feed is complete, the  
resulting reaction product is stirred at about 115°C  
until the pressure within the reactor is constant with  
time, typically about one to 2 hours. The contents of

-23-

the reactor are then cooled to about 95°C and 7216 parts of propylene oxide added at an addition rate of about 1000 parts/hour. When the propylene oxide addition is complete, the reactor temperature is increased to about 100°C, and maintained while stirring for approximately 5 hours or until a constant internal reactor pressure with time is observed.

The contents of the reactor are then heated to about 115°C and a further 2000 parts of ethylene oxide added at an addition rate of about 800 parts/hour. When the feed is complete, the reactor contents are stirred at about 115°C for a further one to 2 hours or until a constant pressure with time is observed.

The potassium content of the crude polyol is removed by treating with magnesium silicate, to give a finished product.

The finished product is characterized in that it has a hydroxyl number of 22.2, a viscosity of 723 cst (25°C), an unsaturation content of 0.087 meq/g and a primary hydroxyl content of greater than 90 percent as observed by nuclear magnetic resonance.

The polyoxyalkylene polyols of Examples 1 to 4 are used to prepare polyurethane elastomers. The elastomers are prepared according to the formulation as given in Table I. Physical properties of the resulting polyurethane elastomers are given in Table II. Comparative elastomers A, B and C are prepared from comparative polyols A, B and C, respectively.

Comparative polyol A is a 2000 equivalent weight linear polyol containing 20 percent by total

-24-

weight ethylene oxide present only as an end cap, and unsaturation of 0.060 meq/g.

Comparative polyol B is a 2750 equivalent weight linear polyol containing 20 percent by total weight ethylene oxide present only as an end cap, and unsaturation of 0.062 meq/g.

Comparative polyol C is a 2000 equivalent weight linear polyol containing 30 percent by total weight ethylene oxide distributed as a 20 percent end cap and internally as one central ethylene oxide block having a molecular weight of 396, and unsaturation of 0.070 meq/g. Comparative Polyol C is obtained by propoxylation of a polyoxyethylene diol having a molecular weight of 400, and subsequently ethoxylating the intermediate product to obtain the final polyol.

-25-

TABLE I

Formulation for Preparation of  
Elastomeric Polyurethane Polymers

		Parts by Weight
5	polyol <sup>①</sup>	88.0
	additional polyol <sup>②</sup>	10.6
	chain-extending agent <sup>③</sup>	10.8
	catalysts <sup>④</sup>	0.5
10	surfactants <sup>⑤</sup>	0.5
	refrigerant-11	7.0
	isocyanate <sup>⑥</sup> index <sup>⑦</sup>	1.0
		(NCO/OH ratio)
15	<sup>①</sup> Polyol, the polyoxyalkylene polyol of Examples 1 to 4 or Comparative polyols A to C.	
	<sup>②</sup> Voranol™ CP 6001, a trifunctional 6000 molecular weight polyether polyol sold by The Dow Chemical Company.	
	<sup>③</sup> 1,4-Butanediol.	
20	<sup>④</sup> Triethylenediamine and dibutyltin dilaurate in a weight ratio of 28:1.	
	<sup>⑤</sup> A silicone surfactant, Tegostab™ B-4113 sold by Th. Goldschmidt Ag.	
25	<sup>⑥</sup> Voranate™ M342, an isocyanate-terminated pre-polymer sold by The Dow Chemical Company, having a 23 weight percent NCO content prepared from 4,4'-diphenylmethane diisocyanate.	
30	<sup>⑦</sup> Total water content of formulation as observed by Karl Fischer titration, about 0.15 weight percent and allowed for when determining amount of isocyanate required at stated index.	

TABLE II  
Polyurethane Elastomers  
(density approximately 600 kg/m<sup>3</sup>)

	Elastomer					Comparative Elastomer		
	1	1-aged <sup>Ⓞ</sup>	2	3	4	A	B	C
<u>Polyoxyalkylene polyol</u>								
<u>Polymer Physical Properties</u>								
Hardness (Shore A)	58	58	63	66	63	70	73	68
Tensile Strength (MPa)	4.8	4.6	4.8	4.7	3.0	4.6	4.7	4.8
Elongation (%)	400	370	385	370	300	350	320	400
Flexural Fatigue (20°C) (cut growth in mm) after 1 x 10 <sup>5</sup> cycles	0.2	0.2	0.4	0.3	1.5	0.2	0.3	0.2
Abrasion Loss (mg)	190	200	180	230	310	300	250	290

<sup>Ⓞ</sup> Physical properties after humid aging of polymer for 7 days at 70°C/95 percent relative humidity followed by 1 day at 70°C in a dry oven.

-27-

As can be seen from the data of Table II, the polymers of this invention prepared with polyoxyalkylene polyols containing internal polyoxyethylene blocks of defined molecular weight display significantly reduced abrasion loss and therefore increased abrasion resistance while maintaining tensile strength, elongation and flexural fatigue properties.

The polymer prepared from polyoxyalkylene polyol 4 exhibits slightly inferior properties but these are most probably due to the polyol's greater equivalent weight and significantly higher unsaturation content.

The improved abrasion resistance of the polymers of this invention is attained through the high ethylene oxide content for their given equivalent weight made possible due to the specific manner of distributing the ethylene oxide within the polyol providing for convenient processing. The abrasion resistance is acquired without apparent detriment to desirable humid aging characteristics of the polymer.

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1. A polyurethane polymer prepared by intimately mixing under reaction conditions an organic polyisocyanate with an isocyanate-reactive composition wherein the ratio of polyisocyanate to isocyanate-reactive composition is such so as to provide an average  
5 of from 0.9 to 1.25 isocyanate groups per active hydrogen atom present in the isocyanate-reactive composition which comprises at least one polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800  
10 to 3000 and containing polymerized ethylene oxide in an amount of from 10 to 40 weight percent by total weight of the polyoxyalkylene polyol and characterized in that

(a) the polyoxyalkylene polyol contains at  
15 least two internal polyoxyethylene blocks having a molecular weight of from 176 to 600; and

(b) the polyol contains a polyoxyethylene end-cap which is from 5 to 25 weight percent of  
20 total polymerized ethylene oxide present in the polyol.

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-29-

2. A polymer as claimed in Claim 1 wherein the internal polyoxyethylene block has a molecular weight of from 220 to 528.

5 3. A polymer as claimed in Claim 1 wherein the internal polyoxyethylene block has a molecular weight of from 308 to 440.

4. A polymer as claimed in Claims 1 to 3 wherein the polyol contains a polyoxyethylene end-cap which constitutes from 15 to 25 weight percent of total polymerized ethylene oxide present in the polyol.

5. A polymer as claimed in Claims 1 to 4 wherein the polyoxyalkylene polyol has an average functionality of from 1.8 to 3.

6. A polymer as claimed in Claim 5 wherein the polyoxyalkylene polyol has an average hydroxyl equivalent weight of from 1000 to 2500.

7. A polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and which comprises polymerized ethylene oxide in an amount of from 10 to 40 weight percent and characterized in that

(a) the polyoxyalkylene polyol contains at least two internal polyoxyethylene blocks having a molecular weight of from 176 to 600; and

(b) the polyol contains a polyoxyethylene end-cap which is from 5 to 25 weight percent of total polymerized ethylene oxide present in the polyol.

-30-

8. A process for preparing a polyurethane polymer having an average density of from 200 to 700 kg/m<sup>3</sup> employing a polymer-forming composition comprising

5 (a) a polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and constituted by polymerized ethylene oxide in an amount of from 10 to 40 weight percent and characterized in that

10 (i) the polyoxyalkylene polyol contains at least two internal polyoxyethylene blocks having a molecular weight of from 176 to 600; and

15 (ii) the polyol contains a polyoxyethylene end-cap which is from 5 to 25 weight percent of total polymerized ethylene oxide present in the polyol;

20 (b) a chain-extending agent, having a molecular weight of less than or equal to 250, in an amount of from 2 to 40 parts by weight per 100 parts by total weight of polyol including (a) present;

25 (c) an effective amount of a blowing agent; and

30 (d) an isocyanate-terminated 4,4'-methylene diphenyldiisocyanate prepolymer in an amount to provide from 0.9 to 1.25 isocyanate groups per isocyanate-reactive

-31-

hydrogen atom present in the polymer-forming composition.

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## AMENDED CLAIMS

[received by the International Bureau  
on 10 September 1991 (10.09.91);  
original claims 1-8 replaced by  
amended claims 1-8 (3 pages)]

1. A polyurethane polymer prepared by  
intimately mixing under reaction conditions an organic  
polyisocyanate with an isocyanate-reactive composition  
wherein the ratio of polyisocyanate to isocyanate-  
reactive composition is such so as to provide an average  
5 of from 0.9 to 1.25 isocyanate groups per active  
hydrogen atom present in the isocyanate-reactive  
composition which comprises at least one polyoxyalkylene  
polyol having a hydroxyl equivalent weight of from 800  
10 to 3000 and containing polymerized ethylene oxide in an  
amount of from 20 to 40 weight percent by total weight  
of the polyoxyalkylene polyol and characterized in that

(a) the polyoxyalkylene polyol contains at  
15 least two internal polyoxyethylene blocks  
having a molecular weight of from 220 to 528;  
and

(b) the polyol contains a polyoxyethylene end-  
20 cap which is from 15 to 25 weight percent of  
total polymerized ethylene oxide present in the  
polyol.

25

3. A polymer as claimed in Claim 1 wherein the internal polyoxyethylene block has a molecular weight of from 308 to 440.

5 5. A polymer as claimed in Claims 1 to 4 wherein the polyoxyalkylene polyol has an average functionality of from 1.8 to 3.

10 6. A polymer as claimed in Claim 5 wherein the polyoxyalkylene polyol has an average hydroxyl equivalent weight of from 1000 to 2500.

15 7. A polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and which comprises polymerized ethylene oxide in an amount of from 20 to 40 weight percent and characterized in that

20 (a) the polyoxyalkylene polyol contains at least two internal polyoxyethylene blocks having a molecular weight of from 220 to 528; and

25 (b) the polyol contains a polyoxyethylene end-cap which is from 15 to 25 weight percent of total polymerized ethylene oxide present in the polyol.

30 8. A process for preparing a polyurethane polymer having an average density of from 200 to 700 kg/m<sup>3</sup> employing a polymer-forming composition comprising

(a) a polyoxyalkylene polyol having a hydroxyl equivalent weight of from 800 to 3000 and constituted by polymerized

ethylene oxide in an amount of from 20 to 40 weight percent and characterized in that

5 (i) the polyoxyalkylene polyol contains at least two internal polyoxyethylene blocks having a molecular weight of from 220 to 528; and

10 (ii) the polyol contains a polyoxyethylene end-cap which is from 15 to 25 weight percent of total polymerized ethylene oxide present in the polyol;

15 (b) a chain-extending agent, having a molecular weight of less than or equal to 250, in an amount of from 2 to 40 parts by weight per 100 parts by total weight of polyol including (a) present;

20 (c) an effective amount of a blowing agent; and

25 (d) an isocyanate-terminated 4,4'-methylene diphenylisocyanate prepolymer in an amount to provide from 0.9 to 1.25 isocyanate groups per isocyanate-reactive hydrogen atom present in the polymer-forming composition.

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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/01240

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : C 08 G 18/48, C 08 G 65/08, A(C 08 G 18/48, 101/00)																	
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC<sup>5</sup></td> <td style="padding: 5px;">C 08 G</td> </tr> </table> <div style="border-top: 1px solid black; padding-top: 5px; margin-top: 5px;">           Documentation Searched other than Minimum Documentation            to the extent that such Documents are included in the Fields Searched <sup>8</sup> </div>			Classification System	Classification Symbols	IPC <sup>5</sup>	C 08 G											
Classification System	Classification Symbols																
IPC <sup>5</sup>	C 08 G																
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category <sup>9</sup></th> <th style="border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">           FR, A, 1450612 (LANKRO CHEMICALS)            26 August 1966            see abstract points 1,2A,4; page 2,            right-hand column, paragraph 4 - page 3,            left-hand column, paragraph 2; page 5,            left-hand column, last paragraph - page            6, left-hand column, paragraph 4; page            6, right-hand column, last paragraph            ---         </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">           FR, A, 2357592 (U.C.C.)            3 February 1978            see claims 1-3,21; page 3, line 25 -            page 4, line 11; page 4, lines 21-35            &amp; CA, A, 1133650            cited in the application            ---         </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,4,7</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">           US, A, 4559366 (F. HOSTETTLER)            17 December 1985            see claim 1; column 10, lines 27-53            ---         </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,7</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">           US, A, 4312973 (F.E. CRITCHFIELD et al.)            26 January 1982            see claim 1; abstract; column 3, line 6            - column 4, line 16            ---         </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,7</td> </tr> </table> <div style="margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> * Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div> </div>			Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	FR, A, 1450612 (LANKRO CHEMICALS) 26 August 1966 see abstract points 1,2A,4; page 2, right-hand column, paragraph 4 - page 3, left-hand column, paragraph 2; page 5, left-hand column, last paragraph - page 6, left-hand column, paragraph 4; page 6, right-hand column, last paragraph ---	1-8	X	FR, A, 2357592 (U.C.C.) 3 February 1978 see claims 1-3,21; page 3, line 25 - page 4, line 11; page 4, lines 21-35 & CA, A, 1133650 cited in the application ---	1,4,7	X	US, A, 4559366 (F. HOSTETTLER) 17 December 1985 see claim 1; column 10, lines 27-53 ---	1,7	X	US, A, 4312973 (F.E. CRITCHFIELD et al.) 26 January 1982 see claim 1; abstract; column 3, line 6 - column 4, line 16 ---	1,7
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X	US, A, 4559366 (F. HOSTETTLER) 17 December 1985 see claim 1; column 10, lines 27-53 ---	1,7															
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<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search            3rd June 1991         </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report            15. 07. 91         </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">           International Searching Authority            EUROPEAN PATENT OFFICE         </td> <td style="border-bottom: 1px solid black; padding: 5px;">           Signature of Authorized Officer  <div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px 10px; margin-right: 10px;">M. PEIS</div> <div style="font-family: cursive; font-size: 1.2em;">M. Peis</div> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search 3rd June 1991	Date of Mailing of this International Search Report 15. 07. 91	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer <div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px 10px; margin-right: 10px;">M. PEIS</div> <div style="font-family: cursive; font-size: 1.2em;">M. Peis</div> </div>											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	FR, A, 1413775 (I.C.I.) 30 August 1965 see abstract points A <sub>1</sub> -A <sub>4</sub> ; page 1, right-hand column, paragraph 2 - page 2, left-hand column, paragraph 3; example ---	1,5-7
A	FR, A, 2491932 (TEXACO DEVELOPMENT) 16 April 1982 see claims 1-5; page 3, line 20 - page 4, line 18 -----	1,8

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9101240

SA 45097

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 08/07/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 1450612		BE-A- 665828	18-10-65
		DE-A- 1570885	12-03-70
		GB-A- 1120223	
		NL-A- 6508073	24-12-65
FR-A- 2357592	03-02-78	US-A- 4125505	14-11-78
		AU-B- 509111	17-04-80
		AU-A- 2670877	11-01-79
		BE-A- 856486	05-01-78
		CA-A- 1105182	14-07-81
		DE-A, C 2730374	12-01-78
		DE-C- 2759334	19-07-84
		DE-B- 2759398	17-07-80
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		JP-A- 56127627	06-10-81
		JP-B- 62039609	24-08-87
		JP-A- 53013700	07-02-78
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		GB-A- 1115151	
		NL-A- 6413173	17-05-65
FR-A- 2491932	16-04-82	None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

